SMI

SORPTIVE MINERALS INSTITUTE

Before the

National Toxicology Program
Board of Scientific Counselors
U.S. Public Health Service

Comments of the

SORPTIVE MINERALS INSTITUTE

on the

Proposed Change in Classification of Silica, Crystalline

December 2 and 3, 1998

1.0 INTRODUCTION

The Sorptive Minerals Institute (SMI) is a national trade association representing the manufacturers and marketers of sorptive mineral products. These products are widely used as pet litters, industrial floor absorbents, agricultural chemical carriers, and other products that provide for a safer environment. Sorptive mineral products produced by SMI members are composed primarily of clay minerals and/or uncalcined diatomaceous earth with minor amounts of accessory minerals. Quartz, a crystalline form of silica, often is present as an accessory mineral.

The National Toxicology Program announced in the Federal Register of October 26, 1998 (volume 26, number 206, pages 57132-57133) that it intends to reclassify Crystalline Silica (Respirable Size) from "Reasonably Anticipated to be a Human Carcinogen" to that of "Known Human Carcinogen."

Based upon a thorough review of the scientific literature and SMI's own research over the past three years, SMI believes that reclassifying crystalline silica as a known human carcinogen is not warranted at this time.

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2.0 REGULATION OF CRYSTALLINE SILICA DUST, INCLUDING QUARTZ

2.1 The Problem in Crystalline Silica Regulation

Despite a large amount of scientific research over many years, quartz and other natural silica phases remain an enigma, especially with respect to their bioactivity. In 1997 the International Agency for Research on Cancer, in a split vote, classified quartz and cristobalite as a known human carcinogen. Despite this classification, IARC's ruling acknowledged that the carcinogenicity of crystalline silica may be related to external factors and that all forms of crystalline silica may not be carcinogenic[1].

> "In making the overall evaluation, the Working Group noted that carcinogenicity in humans was not detected in all industrial circumstances studied. Carcinogenicity may be dependent on inherent characteristics of the crystalline silica or on external factors affecting its biological activity or distribution of its polymorphs."

The link between high exposures to industrially generated quartz dust and the human lung disease silicosis has been known since antiquity. However, during the past few decades research has shown that the quartz dust that causes lung damage is the result of processes that break the quartz into freshly fractured particles that are then immediately respired. These processes include blasting in mines, sawing quartz-containing rocks, concrete and bricks, dry drilling in siliceous rocks, and certain other industrial processes. In these operations, quartz is often a major component of the material. Strict control measures adopted by the responsible operators provide protection for workers.

An exposure to non-fractured quartz in dust appears to be far less of a problem, especially in those materials where quartz is a minor component. In exposures such as mining clay, mining bituminous coal, and the moving and handling of soil, the problems of silica induced lung diseases are absent. The type of quartz found in these operations has geologically aged surfaces and often exhibits a broad range of crystallinity.

Despite these recent findings, regulations continue to be based solely upon research that employed pure, single crystal, recently or freshly fractured grains of quartz of high-temperature origin. This practice has erroneously indicted all quartz particles as being biologically aggressive, including polycrystalline chert and single-crystal grains whose surfaces are occluded by aluminosilicate minerals and/or opaline silica, such as clay or non-crystalline silica.

3.0 THE NATURE OF SILICA

3.1 Complexity of Silica

Crystalline silica is an extremely complex substance. It can vary widely in its degree of crystallinity and in its surface properties. The variation in these properties can have a profound effect on biological activity.

3.2 Ubiquity of Crystalline Silica

Crystalline silica, including quartz, is virtually everywhere in the environment. After feldspar, quartz is the most common mineral in the crust of the earth. Quartz is the principal component in most beach sand and is a major constituent of most soils[2]. Crystalline silica, particularly in the form of quartz, also occurs naturally in the atmosphere with ambient levels up to 1.9 micrograms per cubic meter found in the United States[3].

3.3 Structure of Crystalline Silica

Despite its simple chemical formula, silica (SiO_2) is an exceedingly complex substance[4] which exists in both non-crystalline and crystalline forms. The seemingly simple Si – O bond that, thus far, has defied adequate understanding concerning its ionic or covalent nature illustrates an example of this complexity[5]. Under normal pressures, the basic building block of silica minerals is a silicon atom surrounded tetrahedrally by four oxygen atoms. These tetrahedra have many possible arrangements in space. Some are random or semi-random and cannot build up the three-dimensional periodicity required of a crystalline structure. These are classified as amorphous or paracrystalline. Others are in periodic arrangements, which give rise to various crystal structures.

The various crystalline configurations exhibited by silica are termed polymorphs[6]. The most common polymorphs are quartz, cristobalite, and tridymite with quartz being the most common. The phase diagram in Figure 1 concisely illustrates the pressure and temperature relationship between the various forms of crystalline silica[7]. This diagram shows that, although quartz forms at elevated temperatures, these temperatures are well below the temperatures of formation of tridymite and cristobalite. Most exposures to crystalline silica involve quartz, although cristobalite exposures can occur in limited occurrences.

3.4 Variations in the Crystallinity of Quartz

Petrographic microscopists have long recognized that quartz possesses many degrees of crystallinity. Even conventional X-ray diffraction patterns can show differences. The X-ray diffraction patterns for several quartz varieties[8] appear in Figure 2. These varieties include a National Institute of Standards and Technology ("NIST") quartz, a commercial tripoli, and a chert nodule commonly found in limestone. The NIST quartz standard

consists of well-ordered single crystal fragments of the better-crystallized high-temperature variety. Tripoli and chert are the poorly crystalline, less ordered, authigenic, low-temperature precipitate varieties commonly appearing in sedimentary rocks. A cursory X-ray diffraction examination by investigators with little mineralogical background, however, might conclude that the crystallinity of these three samples would be either identical or not relevant.

Over 20 years ago Murata and Norman[9] carefully examined X-ray diffraction patterns of quartz samples and discovered that a group of five diffraction peaks are diagnostic of the crystallinity. These peaks, appearing at 68° 2θ when using copper Kα radiation are termed the "68° quintuplet." Figure 3a shows the 68° quintuplet for a series of crystallinities for different varieties of quartz. The quartz varieties with the best degree of crystallinity are from high-temperature single crystal grains. Those with the poorest degree of crystallinity are from low temperature, polycrystalline quartz grains. Well-ordered quartz reveals five resolved, distinct X-ray diffraction peaks. Poorly crystallized quartz is defined by increasingly broader and unresolved maxima. Murata and Norman devised a crystallinity index, graphically illustrated in Figure 3b. The crystallinity index, sometimes termed the "Murata ratio," ranges from a normalized 10 for well crystallized varieties to less than 1 for the poorest crystallized, polycrystalline, low temperature material. Asterisks in Figure 2 denote the quintuplet peaks. The dissimilarity of the crystallinity is readily apparent between the well-resolved quartz standard and the tripoli and chert varieties.

Several varieties of quartz can be present in geological deposits. One variety comprises high temperature crystalline quartz in igneous or metamorphic rocks such as granite, gneiss, or schist. This variety also includes grains derived from these rocks through geological processes. This type of quartz has a high degree of crystalline ordering. When transported to a sedimentary deposit during its formation by wind or water, these grains are termed "detrital". Some geological deposits form by weathering of preexisting rocks. The quartz grains that remain after weathering destroys the original rock, *in situ,* are called "residual" grains. They can also have a high degree of crystal ordering. A third variety can form after the original deposition of the clay or its parent minerals. This variety results from precipitation of silica dissolved in the pore water contained in the sediment. These grains are called "authigenic" and normally have a low degree of crystal order.

3.5 Amorphous and Non-Crystalline Silica

Many naturally occurring forms of silica do not have long range periodicity and are not crystalline. These forms include the hydrous silica forms opal-A, opal-CT and opal-C, listed in descending of geochemical abundance. Smith recently made an exhaustive survey of the scientific literature and developed a straightforward nomenclature and classification[10]. He defined opal forms as non-crystalline, hydrated silica. He defined opal as "paracrystalline," indicating that it has limited short-range ordering of six-member

Si—O rings in a disordered matrix. The chemistry of opal also distinguishes it from anhydrous crystalline silica. Paracrystallinity connotes a lack of true crystallinity, and implies only partial ordering in a disordered matrix. *Non-crystalline forms of silica are not considered carcinogenic by IARC, which lists them in class 3.*

The opal forms, including opal-CT, can produce a few X-ray scattering effects falling in the same areas as some of the X-ray diffraction lines of cristobalite. Cristobalite is a biologically active form of crystalline silica formed under conditions of high temperature and pressure (Figure 1). This similarity has often caused opal to be confused with cristobalite. To avoid this confusion, Miles[11] combined two existing NIOSH procedures, 7500[12] and 7601[13] to enable the positive differentiation of opal-CT and cristobalite. Smith found that very few analytical laboratories are aware of the ambiguity between opal and cristobalite in the literature. *Smith also found that these laboratories routinely fail to distinguish between cristobalite, which is regulated, and opal, which is not.*

4.0 NATURE OF THE SURFACE OF QUARTZ

4.1 Importance of the Type of Surface

The reactivity of solid materials is often surface dependent. Therefore, understanding the surface properties of quartz is essential for interpreting its biological activity[14 15 16].

The surface of a solid, as well as its internal structure, can very often determine its chemical activity in a system[17]. Epidemiological studies show this fact is true for quartz. In many cases, the biological activity of a dust is not related to its quartz content. The surface of quartz is the principal factor in its biological activity. Understanding this surface is absolutely essential in interpreting epidemiological data and assessing any risks. The types of quartz surfaces most often considered are freshly fractured, silanol covered, and occluded. The freshly fractured and recently fractured surface appears to be by far the most biologically aggressive. The occluded surface appears to be the least aggressive.

4.2 The Surface of Geologically Aged Surfaces

The surfaces of geologically aged quartz particles have reached equilibrium with their environment and have little or no chemical reactivity. Breaking open a grain of quartz, however, exposes fresh, chemically reactive surfaces. These surfaces have broken chemical bonds that are not easily satisfied within the structure of the quartz crystal because of the rigidity of that structure. These unsatisfied bonds can give rise to free radicals, such as hydroxyl radicals. Spectroscopic measurements have readily detected these free radicals. Chemical changes induced by ambient moisture or water immediately begin to reduce the reactivity of these surfaces. Eventually a new, chemically stable surface results, exhibiting little, if any reactivity.

Fubini[18] and Castranova[19] have measured the nature and abundance of the free radicals produced by fracturing quartz grains (Figure 5, Figure 6). They have also studied the implication of free radicals in biological activity. As the number of free radicals declines, even over as short a period of time as two months, the ability to cause biological damage drops to a very low level.

4.3 The Hydration of the Surface

The inability to generate free radicals results from hydration of the fractured surface. Under ambient conditions the broken bonds resulting from the fracture, and their attendant surface structure, begin to hydroxylate in a stepwise fashion leading to a fully hydrated surface[20] (Figure 5). Although this surface is slightly soluble and will slowly dissolve in water, hydroxylation of the quartz surface proceeds at the same rate, regenerating the hydrated surface. As a result, the ability of a fractured surface to generate and/or present free radicals to either biologic systems or to the environment rapidly vanishes and never reappears.

4.4 Occlusion of the Quartz Particles

Over geologic time, quartz grains in the environment can experience other surface changes. These changes include adsorption of adventitious material such as aluminum ions, magnesium ions, and carbon compounds. Aluminosilicate materials, as well as amorphous hydrated regions can also develop on these surfaces. In some deposits the quartz grains may become intimately enmeshed in clay or opal, forming agglomerates. All of these changes act to further reduce the biological activity of the quartz surfaces. Significantly, these concepts help to explain why exposures to some types of quartz do not lead to silica-related lung disease.

5.0 EPIDEMIOLOGICAL EVIDENCE

5.1 Environmental Epidemiology

Silica-related lung disorders are not pandemic in the general population despite the ubiquitous presence of silica in the environment. Even in dusty and wind-blown arid regions, silicotic problems are isolated and rare. The EPA has provided an excellent summary of the possible environmental exposures leading to silica-related lung diseases[3]. A review of the scientific literature reveals that silica-related lung diseases appear to be most prevalent in workplaces that employ practices that fracture quartz.[1]

5.2 Epidemiological Study in Industries without Silica-Related Lung Diseases

Normally, epidemiological studies target industries that show unusually high incidences of exposure-related diseases. Very few studies cover industries and operations involving quartz with old and/or occluded quartz surfaces due to the lack of silica related lung

diseases. The one study involving the sorptive minerals industry examined the possible health effects of minerals other than quartz. This study, by Zumwalde[21] at NIOSH, investigated the mortality of workers in a sorptive mineral mine and processing facility in south Georgia. Although the clay contained five or more percent quartz, no significant increase in standard mortality rates due to lung cancer or other lung disorders was evident in the workers. The processing of this clay did not involve aggressive crushing, thereby precluding the presence of biologically active fractured grains.

5.3 Epidemiological Studies in Coal Mine Workers

An industry historically under close scrutiny for health problems is bituminous coal mining. Bituminous coal contains geologically aged quartz. IARC Monograph 68 presents a detailed review of the literature[22] relating to this industry. It finds no silica-induced lung cancer associated with bituminous coal mining even though the dust may contain measurable amounts of quartz.

The extensive mixed-dust epidemiological studies of American[23 24], British[25], and European[26] coal mine workers do not always show a direct role for crystalline silica in lung diseases. The data included in these studies show that the surface properties of the quartz present are remarkably similar to those of the quartz found to be present in materials such as sorbent minerals. These coal studies are discussed extensively by Castranova, Vallyathan, and Wallace[16]. The studies show a general correlation between lung disease and coal rank (the carbon-to-hydrogen ratio), rather than quartz content.

In bituminous coal the quartz grains can have coatings of aluminosilicates. Additionally, bituminous coal is soft enough to break around the included quartz grains rather than fracturing them. However, metamorphism through geologic conditions of temperature and pressure can induce changes in the coal beyond merely reducing the amount of volatiles. In anthracite coal, a highly altered "high rank" coal, the coatings on the quartz grains are minimal or absent. Anthracite coal is also sufficiently hard so that quartz grains may fracture when the coal is broken. As a consequence, the quartz in such high rank coals exhibits far greater biological aggressiveness than quartz from lower rank coals.

This situation of quartz in bituminous coal is similar to that of quartz in the minerals used in materials such as sorbent minerals. In both instances the grains have old occluded and/or coated surfaces and are not broken during processing. As a result, the bituminous coal experience lends support to the concept that the quartz found as accessory mineral grains in sedimentary geological deposits does not pose a human health hazard.

5.4 Oil Shale Studies

Some studies have purported to find aggressive biological activity in geologically aged quartz. A study by Holland[27] subjected animals to low dose response, long-term

inhalation experiments using raw and spent domestic oil shale. This study showed a positive response, but the preparation of the shale samples completely compromised the experiment. The samples used in the experiments were ground to ≤5μm prior to being introduced to the animals. The grinding destroyed the geologically aged surfaces and produced abundant freshly fractured quartz surfaces. As a result, this study merely confirmed that freshly fractured quartz is indeed biologically aggressive. Nevertheless, this study eloquently speaks to the point that researchers must fully understand the nature of the raw materials they use in their experiments and the effect that the experimental methods may have on these materials. Failure to do so may produce results that are misleading and, in turn, lead to conclusions that are incorrect.

6.0 CONSIDERATIONS OF THE BIOLOGICAL ACTIVITY OF QUARTZ

6.1 Important Factors

A number of well-qualified investigators have published excellent surveys on the mechanism of the biological effects of crystalline silica. Interestingly, all of these studies involve freshly fractured quartz or cristobalite. Some researchers have begun to investigate the effect of aged or occluded quartz, although the extreme difficulty of separating the grains from the mineral matrix in which they occur without altering their surface makes such studies unusually challenging.

Evidence that varieties of quartz differ in biological activity suggests that many factors are at work. Animals do have many protective strategies, and these factors require examination of the whole animal and not reliance on *in vitro* investigations. The unexpectedly low incidence of silica-related lung diseases in bituminous coal mineworkers has led to several hypotheses concerning the reaction of organisms to quartz. Of particular interest is the role of the aluminosilicate[28 29] occlusions on quartz grains in altering macrophage response to quartz and protecting these cells from premature death.

6.2 Clearance of Particulates from the Lung

The body has several different pathways to clear inhaled particles, depending on the site of their deposition in the respiratory tract[30 31]. Larger particles with a mean aerodynamic diameter of >10μm, deposit in the nasal passages. Sneezing or blowing typically eliminates those that deposit near the front of the non-ciliated epithelium. Those particles deposited in the posterior region of the nasal passages on the mucus-lined ciliated epithelium are swept to the nasopharynx and swallowed. Swallowed particles are eliminated via the gastrointestinal tract. Smaller particles, 3μm to 10μm, impact in the tracheobronchial region and are swept by mucociliary action toward the oral cavity. There they are either expectorated or swallowed. The clearance rate of particles from these two regions is constant and rapid, with half-lives of hours to days.

Particles of 0.5 to 3μm may reach the alveolar region of the lung. Here, particles will be phagocytosed by alveolar macrophages, which then migrate to two locations. One is the ciliated epithelium and then to the oral cavity via mucociliary action. The other is the lymphatic system and eventually to the gastrointestinal tract. Clearance from the alveolar region of the lung can take weeks to months. In circumstances where the particle load in the lung is very high, macrophages become engorged, impairing their ability to phagocytose and migrate. This overload results in the death of the macrophage with the subsequent release of the particles and an expansion of the inflammatory process[32]. In these cases, particles can persist in the lung indefinitely.

6.3 Inflammation

Theories describing silica-induced lung diseases will, in most instances, first consider the inflammatory response to quartz. Inhalation of crystalline silica at inflammatory levels leads to the recruitment and activation of phagocytic cells, and subsequent release of mediators including reactive oxygen species. These inflammatory cell oxidants have two effects that may contribute to the formation of tumors. First, they may cause damage to DNA resulting in mutations. Second, they increase cell proliferation, providing a means for fixing and perpetuating the mutation. Borm and Driscoll[33] have shown that oxidants produced by lung cells as a result of intratracheal dosing with crystalline silica can cause mutations in rat lung epithelial cells. An additional mechanism whereby crystalline silica may cause lung damage is by direct toxicity to DNA. Two studies have shown that crystalline silica can interact directly with DNA, *in vitro*, causing strand breaks[34 35].

The importance of this mechanism in the human disease response remains undefined. Crystalline silica is not very active in most of the standard assays for mutagenic *in vitro* genotoxic effect, supporting the notion that direct damage to DNA may be of secondary importance. Checkoway[36], Holland[27], Lippmann[37], and McDonald[38 39] have published excellent surveys on the biological activity of crystalline silica. All of these studies, however, involve freshly fractured quartz or cristobalite.

The surface of pure quartz that has hydroxylated will contain silanol, Si—OH, groups[40]. These groups have far less activity than free radicals, yet because of their potential acidity, they will have some biological activity. Some investigators have associated hydrogen bonds between the silanol surface and biological membranes, with the loss of membrane integrity.

6.4 Damage to Macrophages

Macrophages that have phagocytized a bacterium, for example, can generate a variety of biological chemicals to destroy it. When a macrophage phagocytizes an inorganic particle, the macrophage will secrete factors promoting fibroblast proliferation and collagen synthesis. Ultimately, when engorged with reactive mineral particles, the macrophage can die, and release even more biologically active chemicals.

Fubini and coworkers extensively discussed the probable fate of macrophages that engulfed silica particles. They emphasize that "... surface radicals may play a specific role in the fibrogenic response to silica ..." They did note that fibrogenic response is possible from milled silica stored for several years. For a laboratory experiment, several years is a long time, but it is the barest fraction of geologic time. The grains of quartz that are found in many materials have surfaces millions of years old, with enough geologic time and weathering for all the free radical activity to have vanished.

Vallyathan has discussed the fate of macrophages that have engulfed mineral particles, including quartz, bentonite (smectite) and kaolin[41]. Although all three minerals showed *in vitro* response, only in quartz was there a progressive granulomatous and fibrotic response *in vivo*. He concluded that *in vitro* responses are not good predictors of fibrogenicity.

6.5 Protection of Macrophages

The lack of silica-related lung diseases among bituminous coal workers suggest that some protective mechanism is at work in the lung. The difference in *in vitro* and *in vivo* results of mineral dusts indicate that extracellular factors are involved. In fact, a particle penetrating deep into the lung will first come in contact with pulmonary surfactant, particularly dipalmitoyl phosphatidylcholine (DPL). These surfactants can coat the particle. Consequently, the macrophage initially will encounter the surfactant and not the mineral surface[28].

Wallace has shown that thin coatings of aluminosilicate clays cover the surfaces of quartz from bituminous coal mines. He has also shown that the pulmonary surfactants will not remove these coatings[29]. Other work has studied the attack of phospholipase A_2, an enzyme associated with cellular membranes and lysosomes, on the DPL layer on both kaolin clay and quartz. The DPL disappears more rapidly on quartz than on kaolin[42]. Both the structure and the chemistry of the kaolin may be responsible. Attachment of the DPL to quartz appears to be through interaction with the trimethylammonium groups[43]. The trimethylammonium groups are probably involved with attachment to kaolin, but interaction of the phosphate portion of the DPL molecule can also interact with the aluminol groups of the kaolin.

A complete understanding of the protection of the macrophages by coatings of clay awaits more research. Nevertheless, the clay coatings and other aluminosilicate adventitious material on the surface of quartz grains, and the adsorption of pulmonary surfactants appear to provide protection for macrophages.

7.0 METHODS OF SURFACE STUDY

7.1 General Considerations

A conventional X-ray diffraction scan of a material can detect if quartz is present. It cannot distinguish among the various types of quartz present. Further, it cannot distinguish between crystalline forms such as cristobalite and certain non-crystalline forms such as opal. Other methods, such as those described by Murata and Norman, need to be engaged for the purpose of regulatory monitoring.

7.2 Variety of Quartz

Many methods exist to distinguish among the varieties of quartz. Each sample or group of samples may require a combination of techniques for complete characterization. A list of possible techniques would include the following:

- A careful X-ray diffraction trace in the region of 68° can establish the internal degree of crystallinity.
- Microscopic techniques can distinguish between freshly fractured angular, single-crystal grains and aged, uncrushed, rounded equant grains.
- Petrographic microscopic investigation can differentiate between single-crystal grains and polycrystalline chert particles.
- Electron microscopy can image small particles and determine their shapes
- EDS techniques can determine the chemical composition of particles imaged by electron microscopy, and can provide information in many cases to presence of surface occlusions.
- X-ray Photoelectron Spectroscopy can provide surface compositional , oxidation state, and structural information of the surface of larger particles
- Low energy electron diffraction can image the surface of larger particles.
- Solution kinetics can detect presence of occluding material on the surface of larger grains
- Sedimentological techniques such as heavy liquid separations can also separate heavier, high temperature single crystal grains from lighter polycrystalline grains.

These techniques, when used by experienced investigators can readily distinguish among the various varieties of quartz.

7.3 Presence of Non-Crystalline Silica

As discussed in Section 3.5, X-ray diffraction cannot unambiguously distinguish between cristobalite and opal. Techniques referenced in the aforementioned section are needed.

8.0 SUMMARY

The SMI believes that the foregoing shows that –

- close examination of the epidemiological evidence does not demonstrate a strong connection between crystalline silica exposure and cancer
- the International Agency for Research on Cancer in its Monograph 68 acknowledges that crystalline silica has varying degrees of biological activity
- a single classification of crystalline silica, especially quartz, regarding biological activity is not possible
- the biological effects of crystalline silica, especially quartz, very strongly depend on surface characteristics and variety of quartz
- methods exist to differentiate the various surface characteristics and varieties
- reclassifying crystalline silica as a known human carcinogen is not appropriate

Crystalline silica is an extremely complex substance and as such, defies a "one size fits all" classification. To make a blanket classification declaring all crystalline silica as a "known human carcinogen" would be to ignore a large body of scientific research and unfairly indict all forms of this common mineral.

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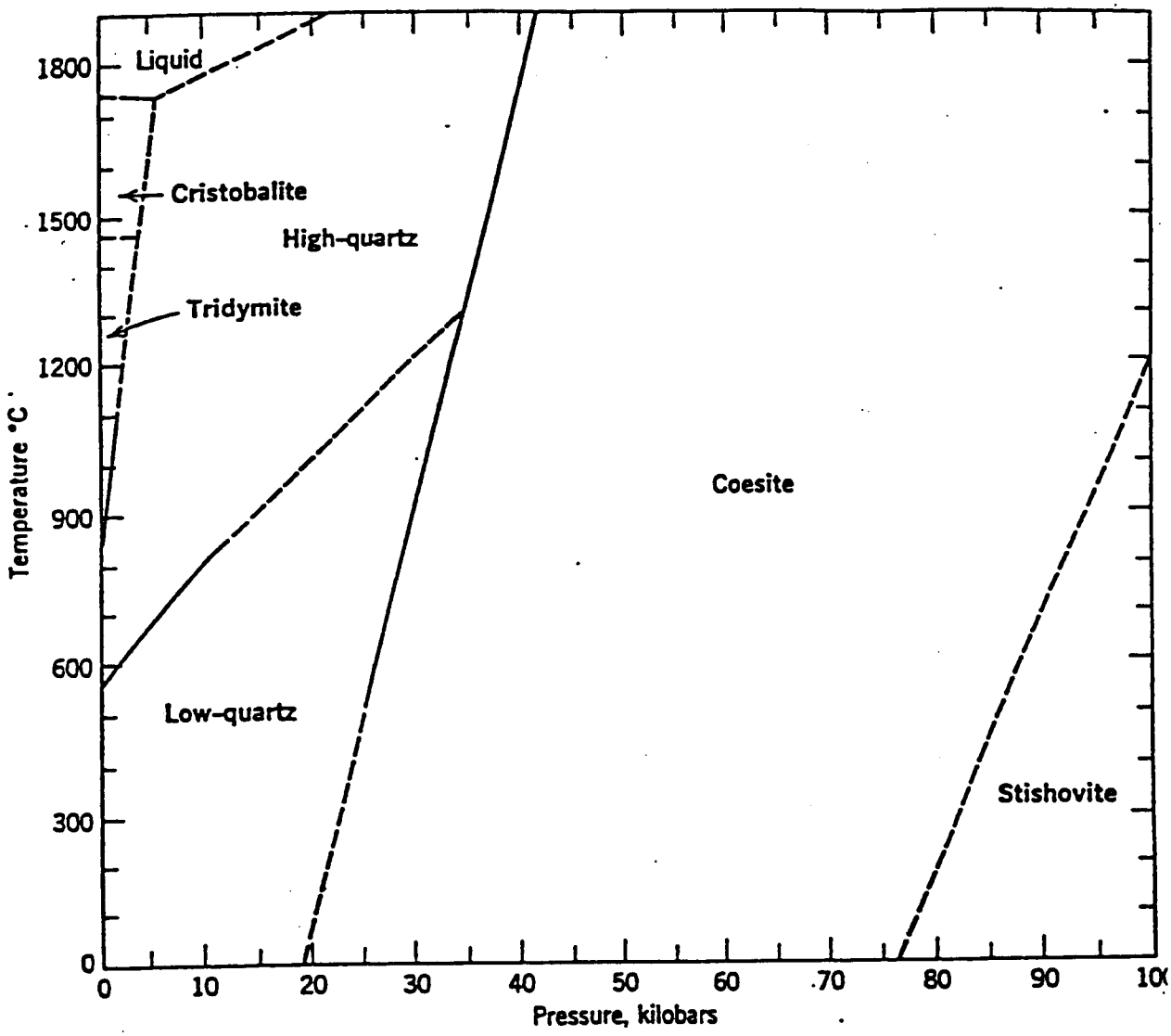
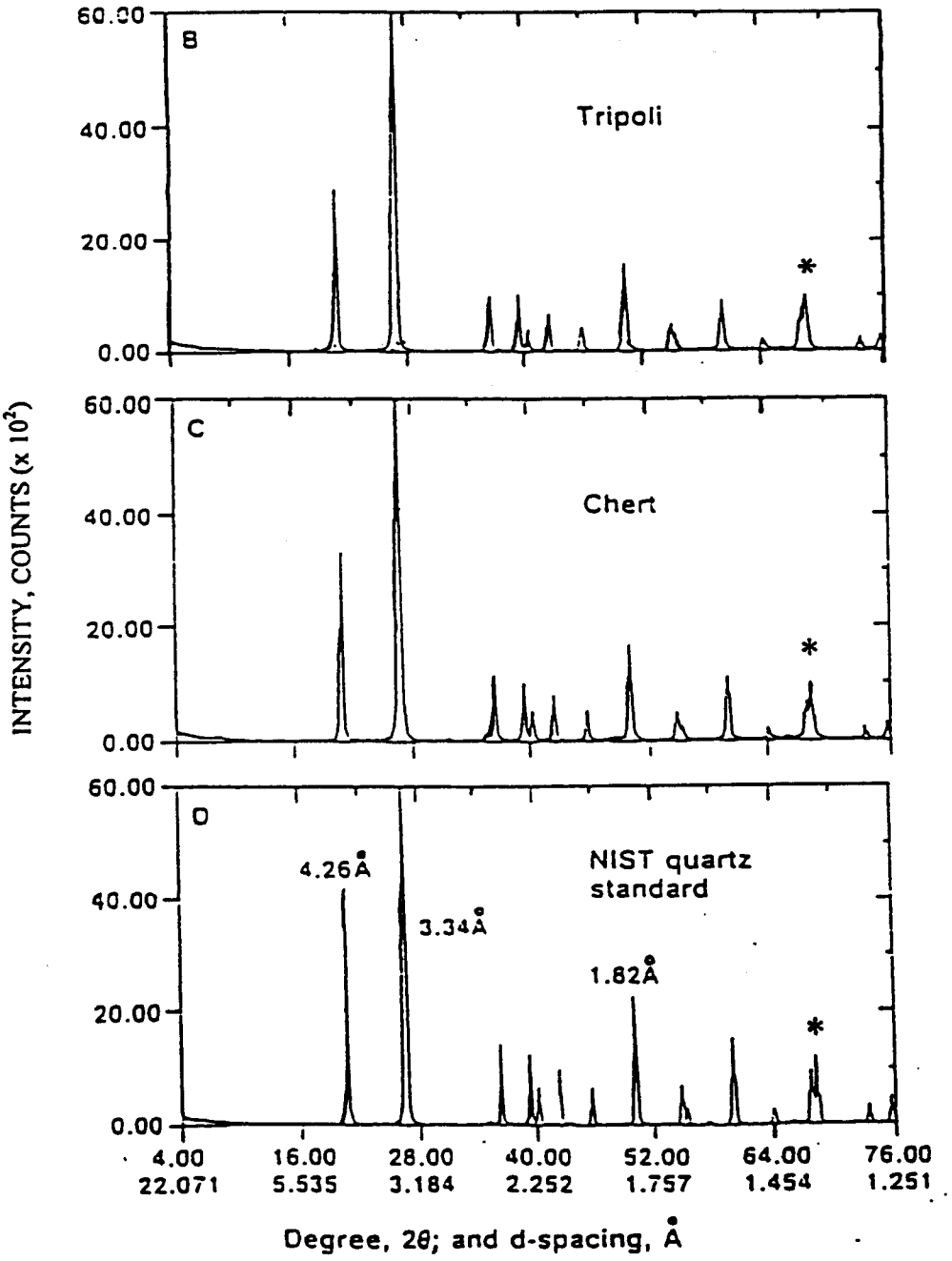
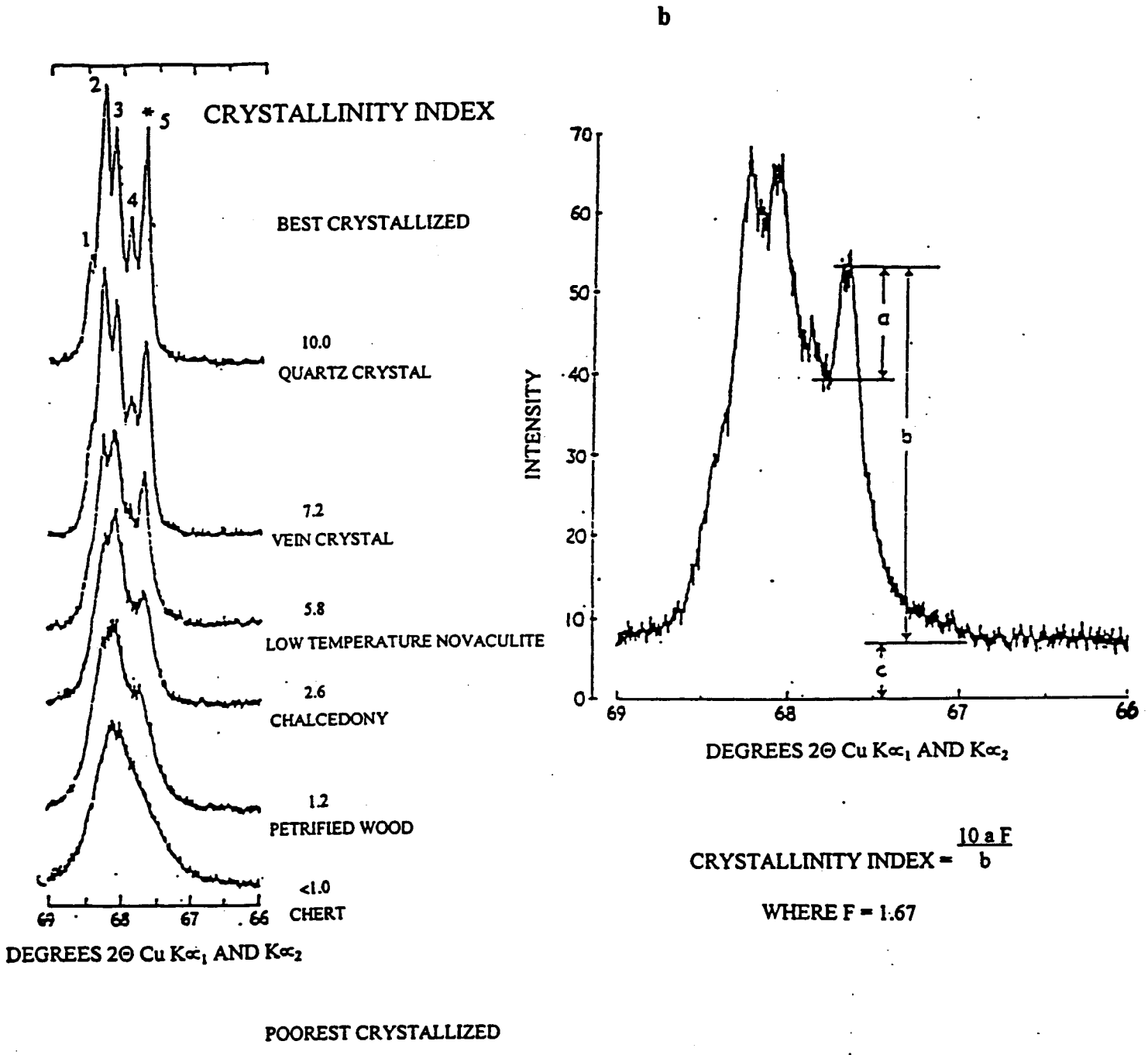


Figure 1 – Phase Diagram for SiO_2, after Klein and Hurlbut[7].



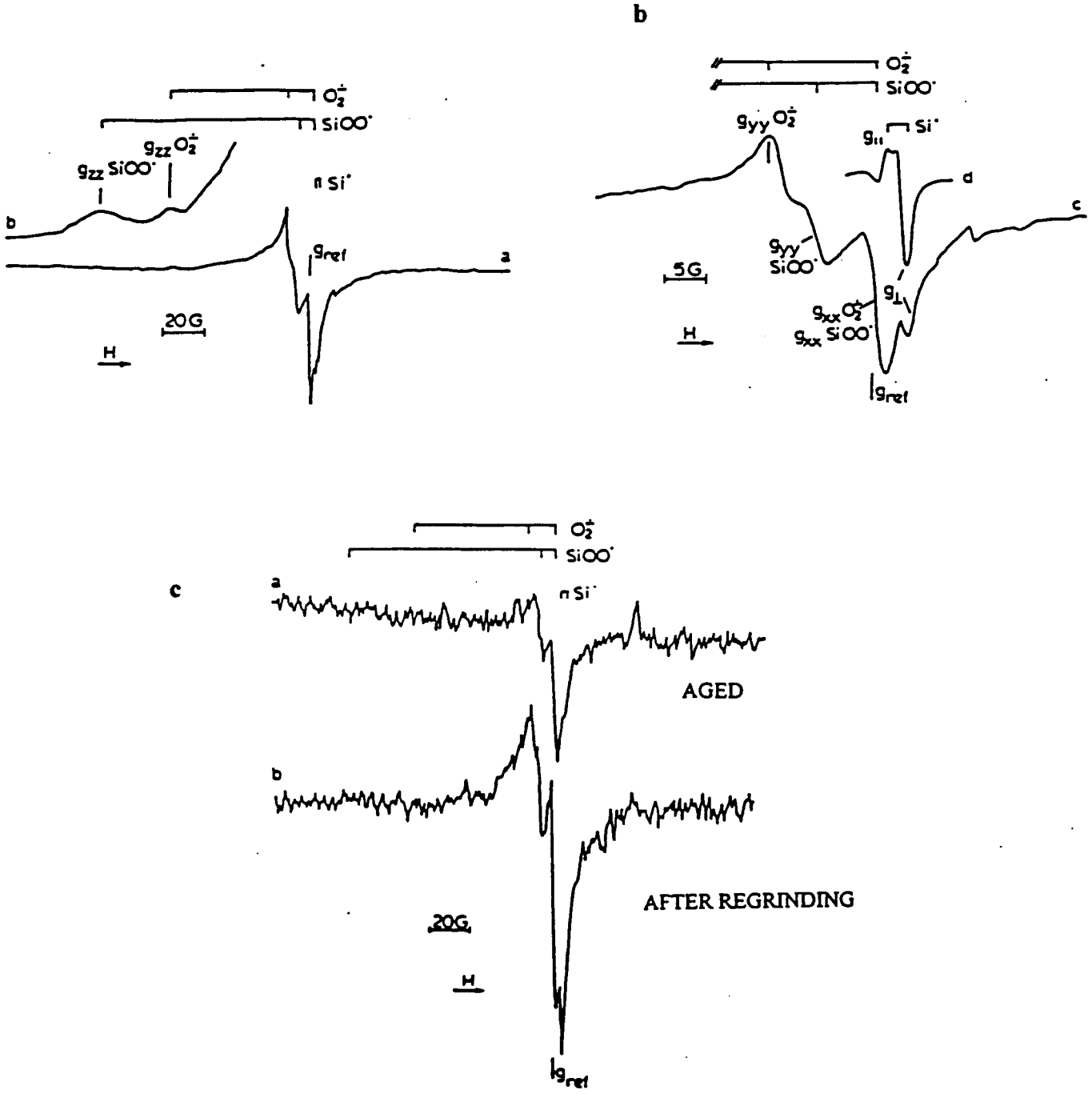
Asterisks indicate the 68° 2Θ quintuplet used in crystallinity index calculations.

Figure 2 – X-ray Diffraction Patterns for Varieties of Quartz, After Ampian and Virta[18].



a = 68° 2Θ quintuplet for varieties of quartz
b = Calculation of the crystallinity index

Figure 3 – Back Reflection Diffraction Peaks as a Function of Crystallinity, After Murata and Norman[9].

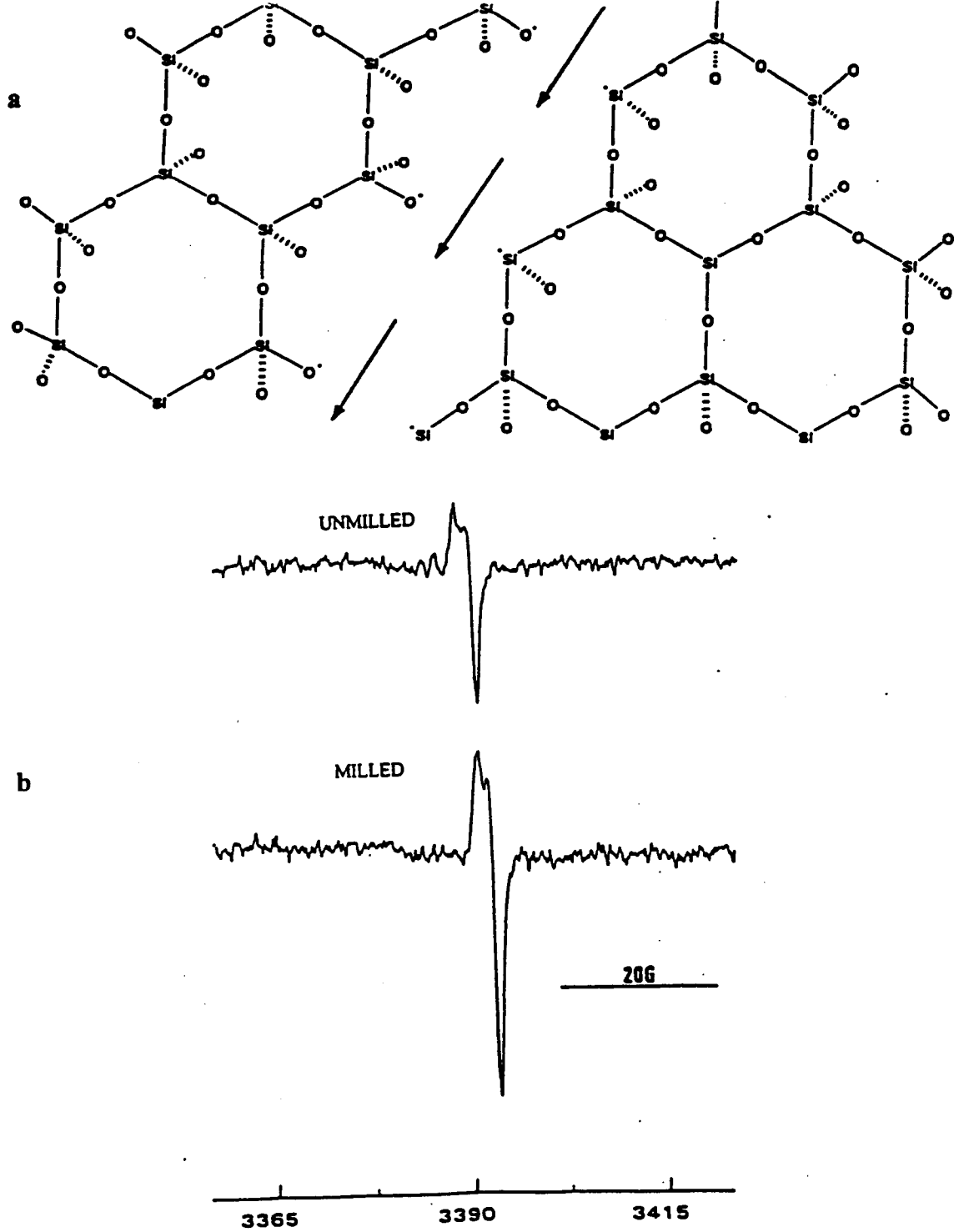


a = Electron spin resonance (ESR) spectrum of pure quartz ground in air, including overmodulation of wings to show details

b = Detail of central portion of spectrum

c = ESR signal of quartz ground several years ago, and after regrinding

Figure 4 – ESR Spectrum of Free Radicals on Quartz Surfaces, After Fubini, Giamello, Volante, and Bolis[18].



a = Mechanism for generating surface radicals through breaking quartz
b = Presence of radicals demonstrated by electron spin resonance (ESR) spectroscopy in milled and unmilled quartz

Figure 5 – Generation of Surface Radicals by Breaking Quartz, After Castranova[10].